

Available online at www.sciencedirect.com

Procedia Engineering 10 (2011) 2833–2838

Engineering
Procedia

ICM11

Effect of voltage on diamond-like carbon thin film using linear ion source

Kim wang ryeol^{a,b}, Park min suk^b, Kim yong whan^a, Jung yong chang^bChung won sub^{a,*}^aDepartment of Materials Science and Engineering, Pusan National University, San 609-735, Korea.^bDongnam Technology Service Division, Korea Institute of Industrial Technology, Busan 618-230, Korea.

Abstract

Diamond-like Carbon(DLC) films were deposited by linear ion source (LIS)-physical vapor deposition method changing the anode voltages from 800V to 1800V, and bias voltages from earth to -200V and characteristics of the films were investigated using Nano-indentation, Micro-Raman Spectroscopy, Field Emission-Scanning Electron Microscope (FM-SEM) and X-ray Photoelectron Spectroscopy (XPS). The results showed that the residual stress and hardness increased relatively with increasing the anode voltage up to anode voltage of 1400V and -100V bias voltage. It was also found that the content of sp^3 carbon was increased with increasing the anode voltage by investigating sp^3/sp^2 ratio through the micro-Raman analysis. From the results, it can be concluded that the physical properties of DLC films such as residual stress and hardness were increased with increasing the anode voltage as 3-dimensional cross-links between carbon atoms and dangling bond are enhanced and the internal compressive stress is also increased with increasing the anode voltage. The optimum anode and bias voltage is considered to be around 1400V and -100V respectively in these experimental conditions.

© 2011 Published by Elsevier Ltd. Open access under [CC BY-NC-ND license](http://creativecommons.org/licenses/by-nc-nd/3.0/).

Selection and peer-review under responsibility of ICM11

Keywords : Linear ion source (LIS); anode voltage; bias voltage; raman spectroscopy

1. Introduction

Diamond-like Carbon(DLC) coatings are characterised by low friction, high wear resistance and high hardness. In mechanical engineering, low friction signifies a lower loss of energy, higher reliability and a better wear resistance. Nowadays, DLC film applied industrial in various field such as, bio technology, mold, tools, mechanic parts etc.[1]~[3]. DLC have amorphous structure unlike diamond and graphite. The bonding structures are included that sp^3 (diamond-like or tetrahedral bond), sp^2 (graphite-like or trigonal bond) and sp^1 hybridization C-C bond. DLC thin films have adjust comparative ratio of bonds,

and it show with a characteristic various by a lot of differences to a physical chemical property of matter to this through deposition method or process variables. DLC coating's researches have announced various deposition methods such as ion plating, Chemical Vapor Deposition(CVD) used DC or RF power supply, sputtering by ion beam and thin film was composite by laser ablation. However these deposition methods were decreased Productivity and showed lower mechanical properties such as adhesion and hardness cause by lack of ion's straight and density about deposition area was too small.

Linear Ion Source (LIS) to use thin-film deposition to the methods existing deposition compared to how long the process of coating also discharge current value of this constant stability and 95% of the attributes of a uniform thin film, and can reproduce the square at the way the circle you using existing source, unlike the high hardness and low friction coefficient of a thin film of DLC coating possible advantages for the area.

This research was deposited DLC thin film using by the LIS with Physical Vapor Deposition (PVD) on substrate and put inside two gases in chamber such as acetylene (C_2H_2) and argon (Ar). Thin film deposition conditions as anode voltage to 800V changing to 1800V and bias voltage from earth to -200V, the resulting bonding strength and hardness, residual stress and combined structure as well as research by thin-film coating for optimum condition for.

2. Experimental

The substrate material was an AISI 4140. After a Cr interlayer of 400nm was deposited by sputtering, DLC thin films with various voltages were deposited by linear ion source. These films are prepared by the process setting at flow rate of 60sccm C_2H_2 , 0.6A current to obtain 0~1800V, earth~-200V using various anode voltage and bias voltage. Structures of DLC thin films were characterized by micro raman spectroscopy with an He-Cd laser wavelength 633nm in the wave number range 1000~2000 cm^{-1} . Also, the films were characterized by X-ray Photon Spectroscopy (XPS) using a Al source operating at 200W beam power. The thickness measured by nano indentation of MTS. The cross section of the specimens were studied by Field Emission-Scanning Electron Microscopy (FE-SEM).

Figure 1 shows the LIS system. In the LIS, ionized gas between the cathode and the anode through the gas flow, anode voltage was applied to the anode side. This voltage was high electromagnetic fields between the inner and outer coils maintained plasma state. The plasma state ions are thrown by the anode electromagnetic ion beam the ions to deposited the surface of the material. The DLC thin films were deposited by this system. This LIS have two basic ion source geometries, commonly called end-drift and closed-drift mode-layer design. Both originated from research in electric space propulsion which pioneered in the former Soviet Union and later adopted for industrial use by Kaufman et al and others. A special case of ion assistance with a conventional magnetron configuration is when negative ions are involved. [16]

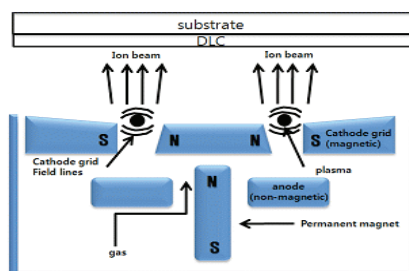


Fig. 1 Diamond-like Carbon(DLC) films were deposited by Linear Ion Source(LIS)-physical vapor deposition method in different various conditions

3. Results

3.1. Microstructure of DLC thin film with varied anode voltage and bias voltages.

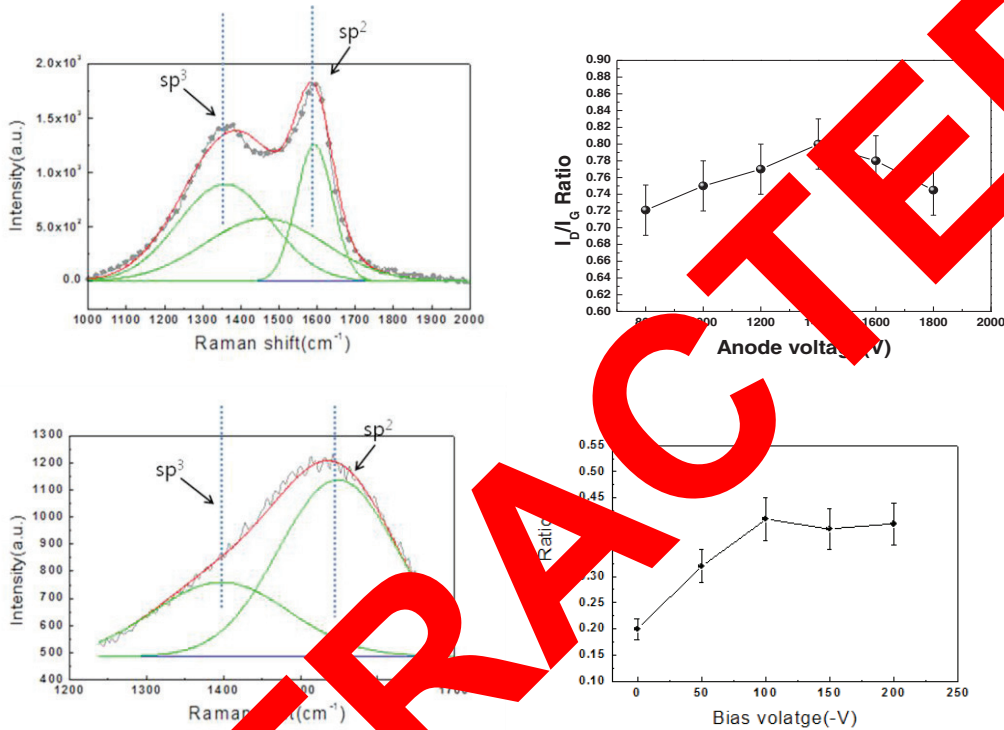


Fig. 2. (a) The deconvolution of micro raman peaks of DLC films : anode voltage(1400V) (b) I_D/I_G ratio with varied anode voltage (c) The deconvolution of micro raman peaks of DLC films : bias voltage(-100V) (d) I_D/I_G ratio with various bias voltages

Fig.2. shows the Raman spectra of the thin films with anode voltage's range from 800 to 1800V and bias voltage from 0V to -250V. DLC films consist of amorphous carbon with short and medium range ordering of sp² and sp³ bonds with the characteristics raman peaks. Raman scattering is usually used to identify the structural arrangements of the carbon atoms.[7] It consists of two peaks located at 1570 cm⁻¹, labeled as G(graphite) band, and 1360 cm⁻¹, labeled as D(disorder) band. The G-peak is due to the in-plane stretching of all pairs of sp² atoms in rings and chains. The D-peak is due to the breathing modes of sp² atoms in rings. The Raman spectra were deconvoluted with Gaussian line fitting and the fitted parameters were used to calculate the Raman parameters, including the band position, bandwidth and spectra intensity ratio I_D/I_G . Ferrari and Robertson [8] suggested that the graphite-like sp² clusters reduce in both number and size as the I_D/I_G decreases. An increasing I_D/I_G ratio correlated with an increase in the graphite-like nano-crystallite, while the shift in the G band position toward lower wavenumbers can

reveal an increase in diamond-like characteristics.[5] Fig.2. (b) shows the result of raman spectroscopy at anode voltage 1400V and I_D/I_G ratio from 800 to 1800V. I_D/I_G ration is the highest at 1400V then sp^3 has the highest proportion. These results also confirm by the XPS analysis later. Fig.2.(d) shows the raman spectra of variable bias voltage from earth to -200V. And in case of bias voltage that the highest I_D/I_G ratio voltage was -100V.

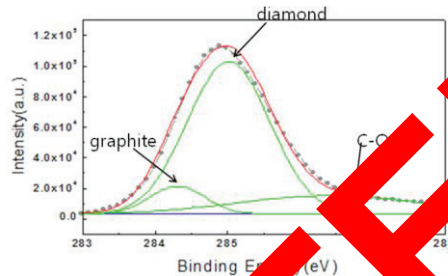
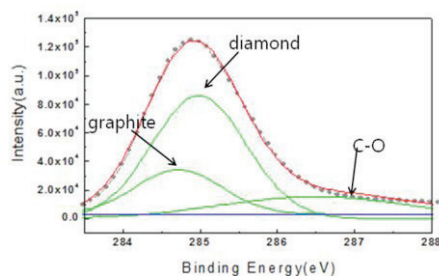


Fig. 3. (a) The deconvolution of XPS C1s peaks of DLC films : anode voltage (1400V) (b) bias voltage(-100V)

Fig. 3. is the XPS spectra of the DLC films with Ar and C2 at 1400V anode voltage and -100 bias voltage respectively. The XPS analysis results of C1s core level spectra of DLC films at 1400V anode voltage and -100 bias voltage. The spectrum of C₂H₂ DLC film is more symmetric than the others two spectra. The XPS spectra are fitted by three peaks of Gaussian distribution centered at 284.0, 285.1 and 287.5 eV, belonging to sp^2 , sp^3 and C-O bonds, respectively. [7] The spectra of the films deconvoluted using by Gaussian fitting. And sp^3 fraction was calculated as follows ; the relationship between D-peak's area and G-peak's area

$$\%sp^3 \text{ fraction} = \frac{D_{FA}}{D_{FA} + G_{FA}} \times 100 \quad (1)$$

Raman spectroscopy based on the analysis showed the biggest difference in 800V and 1400V anode voltages. sp^3 fraction was calculated as 75% at anode voltage 1400V. 3% higher than 800V the results showed. Likewise, bias voltage, sp^3 fraction was calculated as 89% at -100V. sp^3 fraction was highest when the 1400V and -100V, which is consistent with previous Raman spectroscopy results of the analysis showed.

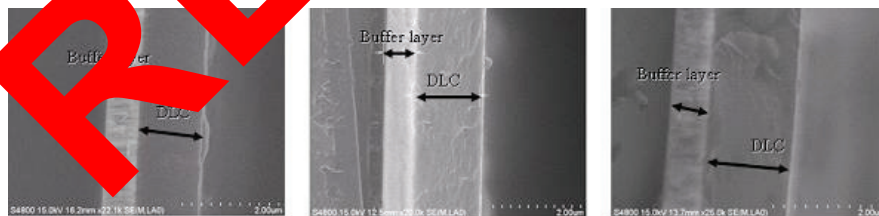


Fig. 4. Field Emission-Scanning Electron Microscope(FE-SEM)image for deposited DLC film. (a)anode voltage 800V, (b)1400V, (c)1800V

Fig. 4. shows an FE-SEM image of cross-sectional with DLC thin films at various conditions. Depending on the thickness of the dynamics of the voltage difference can be observed that I have. The thickness of thick detachment could occur easily, but could be observed. The following comparison of the hardness and the mechanical properties can be determined that a bad thing, because the residual compressive stress is thought.

3.2. Mechanical property of DLC thin film with varied voltages.

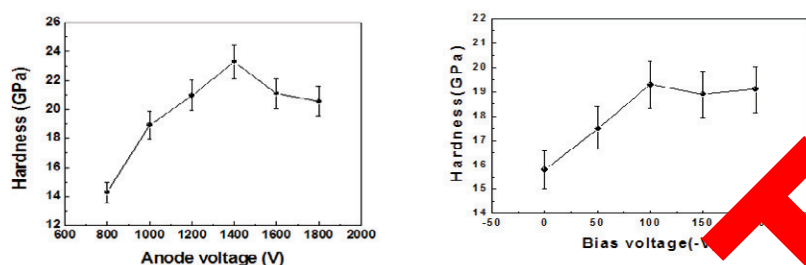


Fig. 5. Hardness of DLC thin film deposited with different voltages. (a) anode voltages (b) bias voltage

The hardness was measured by nano-indentation with various variables such as anode voltage and bias voltage. A commonly accepted rule of thumb suggests that the substrate independent measurements can be obtained if the indentation depth is kept to less than 10% of the film thickness. In our case, according to this rule, nano-indentation on cross-sections of 1.5μm films would have to be made at a penetration depth of less than 150nm. As a result, the highest hardness is about 23GPa at anode voltage 1400V and about 19.5GPa at bias voltage -100V. From the results of Raman and XPS analysis, it is evident that the increase in nano-hardness is due to the increase in the amount of sp³ C-C bonds in DLC films.

4. Conclusion

The fraction of sp³ bonds in the DLC film increases with anode voltage up to 1400V and decreases with anode voltage above 1400V and bias voltage up to -100V; The amount of sp³ bond is maximum at the anode voltage of 1400V and bias voltage of -100V. The hardness of the DLC thin film are maximum at the anode voltage of 1400V and bias voltage of -100V which is consistent with the results from the structural analysis of the film. As voltages increases, kinetic energy to push carbon ions from LIS increases. The carbon ions with high kinetic energy are combined with dangling bonds and form three dimensional cross-links, which improves the mechanical properties of the DLC thin film. The sp² bond is developed at the anode voltage above 1400V and bias voltage about -100V. This increased sp² bond relieves the distortion of bonding length and angle and makes the non-uniform deposition, causing residual stress, ion density, and hardness to decrease due to the reduced amount of 3-dimensional interlink. In conclusion, the optimal anode voltage for DLC film deposition on substrate using LIS-PVD is 1400V, -100V in these experiments which produces the highest hardness.

References

- [1] J. Robertson, *Mater. Sci. Eng.*, R 37 (2002) 129.
- [2] J. Robertson, *Surface and Coating Technology*, 50 (1992) 185.
- [3] K.-R. Lee, K. Y. Eun, *Bull. of the Korean Inst. of Met. & Mater.*, 6(4) (1993) 345.
- [4] K.-R. Lee, K. Y. Eun, I. Y. Kim, J. R. Kim, *Thin Solid Films*, 377-378 (2000) 261.
- [5] C. K. Lee, *Diamond & Related Materials*, 17 (2008) 306.
- [6] D. Sheeja, B. K. Tay, K. W. Leong, C. H. Lee, *Diamond & Related Materials*, 11 (2002) 1643.
- [7] S.M. Chiu et al. / *Journal of Alloys and Compounds* 449(2008)379~383
- [8] A.C. Ferrari, J. Robertson, *Physics. Rev. B* 61 (2000) 14095
- [9] S. Chowdhury, M.T. Laugier, I.Z. Rahman, *Thin Solid Films* 468 (2004) 149
- [10] J. C. Angus, P. Koidl, S. Domitz, *Plasma Deposited Thin Films*, CRC Press, Boca Raton, FL (1986)
- [11] H. Tsai, D. B. Bogy, *J. Vac. Sci. Technol.*, A5(1987) 3287.
- [12] D. Nir, *Thin Solid Films*, 112 (1984) 41.
- [13] M. David, R. Padiyath, S. V. Badu *AIChE J.*, 37(1991) 367.
- [14] K. Enke, *Thin Solid Films*, 80 (1981) 227.
- [15] J. W. Zou, K. Schmidt, K. Reichelt, B. Dischler, *J. Appl. Phys.*, 67 (1990) 1000.
- [16] A. Anders / *Surface & Coating Technology* 200 (2005) 1893-1906